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SEMI-OPTICAL LINES IN THE X-RAY SPECTRA*

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ABSTRACT. In this paper an attempt has been made to sort out some lines in the K, L, and M series of X-ray spectra which are somewhat different in character as regards their origin and have a peculiarity of their own. Such lines belonging to the K series are K_{β_1}, K_{β_3} and K_α ; to the L series are L_α, L_{β_2}, L_{β_6}, L_{γ_1}, L_{γ_4}, &, L_{γ_6} and to the M series are M_{α_1}, and ($M_{III} \leftarrow O_{IV}$), only for some particular elements in each of the series as mentioned in the paper. ν/R values of the final states of these lines have been shown to accord reasonably with those of the lines themselves. An attempt has, therefore, been made to bring out the analogy between the transitions of these lines with those of optical lines from the fact that a knocked out electron from an inner level of an atom goes to a vacant, partially vacant or optical level and then a transition from one of these levels gives rise to them. Hence the name ' semi-optical.' Also, available experimental facts have been put forward in support of the view adopted.

INTRODUCTION

The first idea of semi-optical lines in the X-ray region was developed by Backlin, Siegbahn and Thoraeus.[1] They plotted the wave-length difference between K_{α_1} ($K \rightleftharpoons L_{III}$) and K_{β_1} ($K \rightleftharpoons M_{III}$) against atomic number from Na (11) to Sc (21) and their curve began bending from S (16) and sloped down from Al (13) to Na (11). K_{β_1} is the transition from M_{III} level to K level. It has a faint component K_{β_3} ($K \rightleftharpoons M_{II}$) which is resolved for heavier elements beginning from Rb (37).

According to Stoner and Smith's model of electron structure of atoms, M_{II} level is completely filled up at Si (14) and M_{III} level at Ar (18). The M_{III} level begins to develop first from P (15). So the question of obtaining the K_{β_1} lines for Na (11), Mg (12), Al (13) and Si (14) becomes certainly curious. Similarly a plot of the wave-length difference between K_{β_1} and K_{β_5} ($K \text{——} M_{IV}\, M_V$) (a forbidden

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transition and called K_{β_2} in the paper of the authors mentioned) against atomic number from K (19) to Cu (29) also showed an abrupt discontinuity of the curve at Sc (21) and it sloped down to K (19). There is no electron at all in $M_{IV}M_V$ level for K (19) and Ca (20). Thus the K_{β_1} lines for Na (11) to Si (14) and K_{β_5} lines from K (19) to Sc (21) were called semi-optical lines by the authors [1] mentioned above. Their idea was, that these lines were due to transitions of electrons from virtual optical levels. But an optical or virtual level must have an electron before it can serve as an initial state for the emission of a quantum. No further explanation for calling these K_{β_1} and K_{β_5} lines as semi-optical for the particular elements mentioned above was given.

A number of such semi-optical lines in the K, L, and M series of X-ray spectra have been selected and some possible explanations of their origin and the reason for calling them so have been attempted with the available experimental data.

SOME GENERAL CONSIDERATIONS AND DISCUSSION

An optical line of an atom originates, as we all know, when the valence electron of the atom is raised up to a higher virtual level or higher quantum state by the absorption of energy and then falls back to its initial level or some other level of lower quantum state, the transition being generally governed by the rules of selection. On the contrary, a true X-ray line arises when an electron from a particular inner level (say K) is knocked out of the atom by the absorption of energy, it being unable to go to other inner levels of the atom if these are completely filled up with their proper share of electrons, and another electron from some other filled up level jumps to the K level giving rise to a K emission line. The transition also in this case is governed by the rules of selection. Thus in the case of X-ray spectra the atom is first of all ionised in the inner level.

Now, let us call the last completely filled up level of an atom the periphery or the boundary of the atom. After the periphery lie the optical levels of the atom. Kossel's theory explained that the principal limit (say—, K or L) corresponds to the energy of transfer of an electron from the K or L level to the outside of the atom or to the first unoccupied orbit and the extended structure of the principal limit due to the transfer of the electron to the optical levels. But recently the theory of the extended structure of the principal limit has been modified by Kronig.[2]

That the main absorption limit or edge of an inner level of an atom might be due to the ejected electron from the inner level coming to rest in

the first unoccupied or partly occupied level, may be postulated if the energy $\left(\text{or } \frac{\nu}{R}\right)$ value of the corrresponding emission line (the transition from the first unoccupied or partly occupied level to the particular inner level) agrees with the main absorption limit of that particular inner level. In explaining the origin of the L_{II} and L_{III} principal limits for the elements Lu (71) to Au (79) Sandstrom [3] showed that the ν/R values of the L_{II} limits and L_{III} limits of those elements were equal to those of the L_{γ_6} [$L_{II} \rightleftharpoons O_{IV}$] and L_{β_5} [$L_{III} \rightleftharpoons O_{IV}\, O_V$] emission lines of the elements [Lu (71) to Au (79)] within the limits of experimental error. We must, therefore, infer that the emission of L_{β_5} or L_{γ_6} is exactly analogous to that of a resonance line in the optical region. L_{β_5} is due to the transition from $O_{IV}\, O_V$ to L_{III} level and L_{γ_6} is due to that from O_{IV} to L_{II}. But the O_{IV}, O_V levels are in a state of development from Yb (70) and are completely filled up with electrons at Au (79). So the knocked out electron from L_{II} or L_{III} level of each of these elements, instead of going beyond the periphery of the atom, goes to the O_{IV} or O_V levels. Then, these X-ray lines (having transition from O_{IV} or O_V to L_{II} or L_{III}) for the elements Lu (71) to Au (79) may, therefore, be called semi-optical lines. Similar is the case with L_{β_2} ($L_{III} \rightleftharpoons N_V$) and L_{γ_1} ($L_{II} \rightleftharpoons N_{IV}$) for the elements from Zr (40) to Ag (47), where the N_{IV} N_V levels are in a state of development and with L_{γ_4} ($L_I \rightleftharpoons O_{II}\, O_{III}$) from In (49) to Xe (54) where the O_{II} O_{III} is also in a state of development. Detailed results for these are given below.

L Series :

Figure 1 is a plot of the wave-length difference between L_{α_1} ($L_{III} \rightleftharpoons M_V$) and L_{β_2} ($L_{III} \rightleftharpoons N_V$) against atomic number from (40) to (57).

The nature of this curve is similar to that of the wave-length difference between K_{α_1} ($K \rightleftharpoons L_{III}$) & K_{β_1} ($K \rightleftharpoons M_{III}$) against atomic number from (11) to (20) as shown by Backlin, Siegbahn and Thoraeus [1] mentioned in the earlier part of the paper. Figure 2 shows the same thing for L_{γ_1} ($L_{II} \rightleftharpoons N_{IV}$) when the wave-length difference between L_{β_1} ($L_{II} \rightleftharpoons M_{IV}$) and L_{γ_1} is plotted against the corresponding atomic numbers.

In explaining the origin of the L_{II} and L_{III} absorption limits of the elements [(70) to (79)] Sandstrom [3] has shown that the ν/R values of the L_{II} and L_{III} limits of these elements agree satisfactorily with those of L_{γ_6} and L_{β_5} as has already been mentioned. Kawata [4] has also experimentally shown that the L_{β_5} lines of W (74) and Pt (78) are strongly absorbed on passing through an

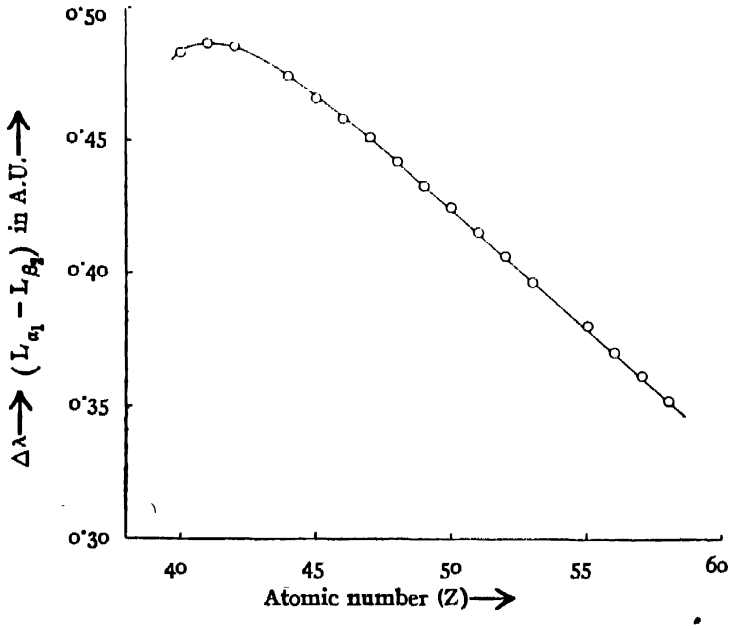


FIGURE 1.

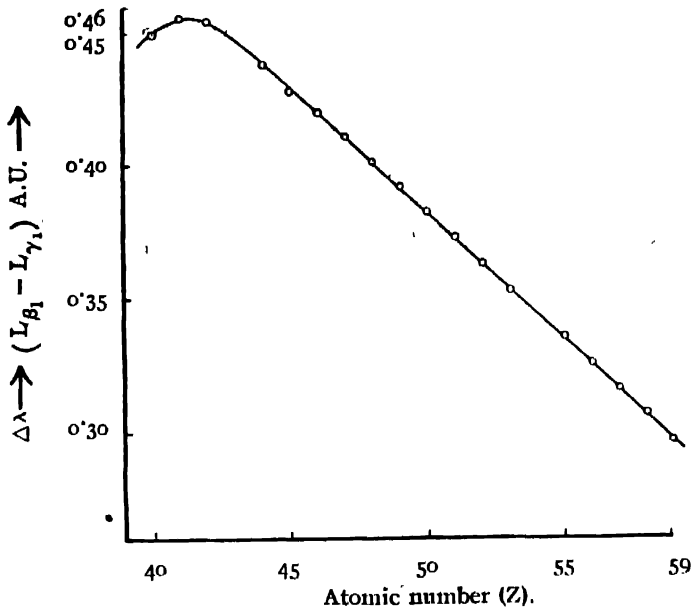


FIGURE 2.

absorption screen of W (74) and Pt (78). Figure 3 shows the relation between the difference between ν/R values of L_{III} and the ν/R values of L_{β_2} lines against atomic number. Figure 4 shows the same thing for L_{γ_1}.

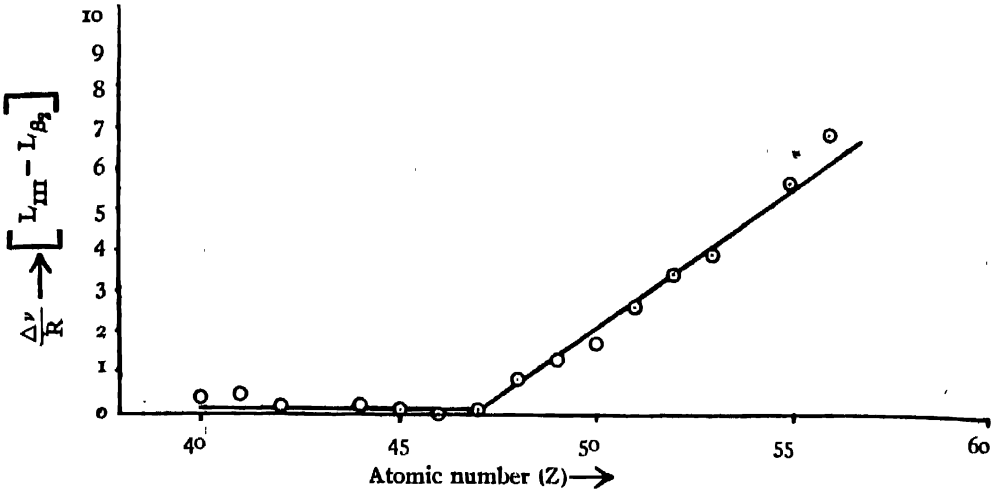


FIGURE 3.

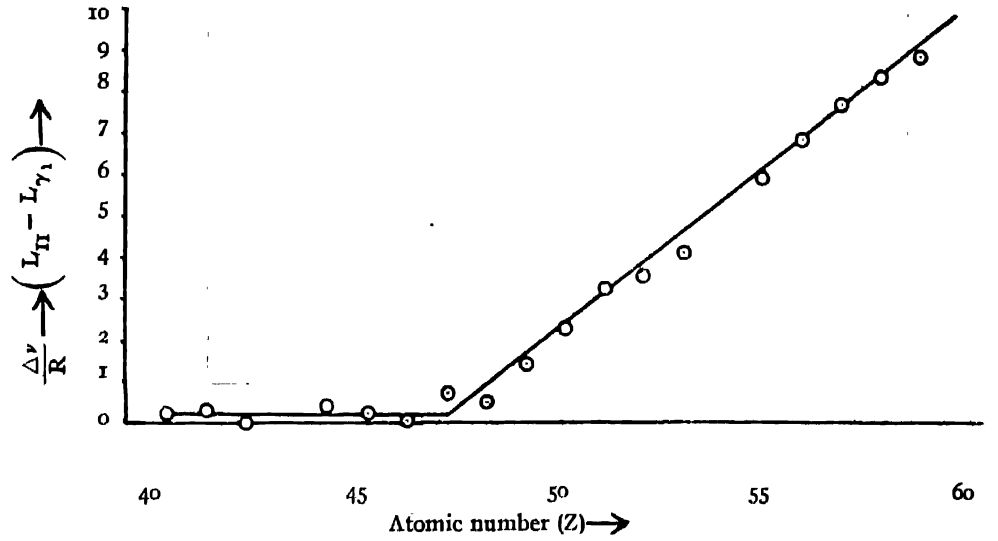


FIGURE 4.

In tables I and II, are given these values for L_{β_5} from elements Lu (71), of L_{β_2} from Zr (40), of L_{γ_1} from Zr (40), of L_{γ_4} from In (49). In each of these cases the ν/R values of the principal limits agree with those of the corresponding lines within the limits of experimental error, for the elements whose particular levels, serving as initial states of the lines, are in a state of development. This means, say, as in the case of L_{β_5}, the knocked out electron from the L_{III} level of

any element beginning from Lu (71) to Au (79) goes to the $O_{IV}O_V$ level which is in a state of development for these elements.

TABLE I.

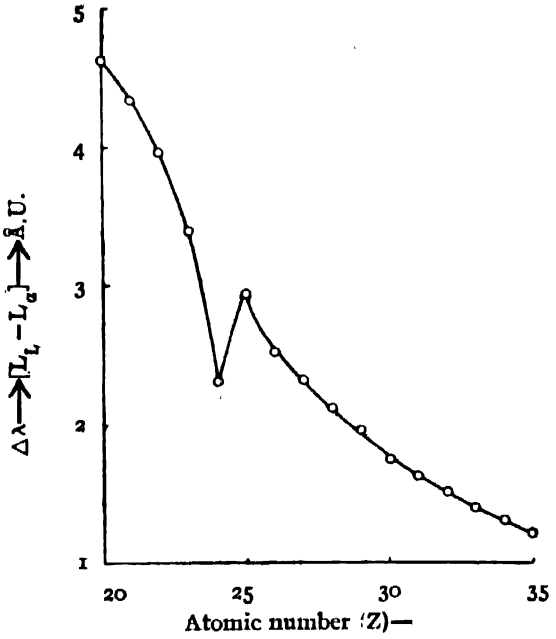
Atomic number (Z).	Number of electrons in O_{IV}, O_V level.	$\frac{\nu}{R}$ for L_{β_5} ($L_{III} \leftarrow O_{IV}\ O_V$)	$\frac{\nu}{R}$ for L_{III}	Difference between L_{III} and L_{β_5}.	Remarks.
71	1		681·24		All experimental values, except where mentioned, are taken from Siegbahn's Spectroskopic Der Röntgenstrahlen, 2nd Ed., 1931.
72	2		704·77		
73	3	727·15	728·0	+ 0·85	
74	4	751·32	751·30	− 0.02	
75	5 or 6	775·75	775·21	− 0·54	
76	6 or 7	799·6	800·04	+ 0·44	
77	7 or 8	825·75	825·60	− 0·15	
78	9 or 10	851·48	850·89	− 0·59	
79	10	877·65	877·70	+ 0·05	
80	10	905·21	904·53	− 0·68	Difference goes on increasing with atomic number as shown in Sandström's curves for L_{β_5} and L_{γ_6}.
81	10	931·30	931·98	+ 0·68	
Atomic number.	Number of electrons in N_{IV} N_V level.	$\frac{\nu}{R}$ for L_{β_2} ($L_{III} \leftarrow N_V$)	$\frac{\nu}{R}$ for L_{III}	Difference between L_{III} and L_{β_2}.	
40	2	163·48	163·87	+ 0·39	
41	4	174·37	174·84	+ 0·47	
42	5	185·59	185·81	+ 0·22	
43	6				
44	7	208·92	209·12	+ 0·20	
45	8	221·07	221·27	+ 0·20	
46	10	233·62	233·63	+ 0·01	
47	10	246·69	246·76	+ 0·07	Difference goes on increasing with (Z) as shown in Fig. 3.
48	10	259.89	260·71	+ 0·82	
49	10	273·56	274·85	+ 0·129	

TABLE II.

Atomic number (Z).	Number of electrons in N_{IV}, N_V level.	$\frac{\nu}{R}$ for L_{γ_1} ($L_{II} \rightarrow N_{IV}$.)	$\frac{\nu}{R}$ for L_{II}.	Diff. between L_{II} and L_{γ_1}.	Remarks.
40	2	169·58	169·83	+0·25	
41	4	181·35	181·6*	+0·25	*These values are taken from Sommerfeld's Atomic structure and spectral lines (Vol I), Revised, 3rd Ed. (1934)
42	5	193·43*	193·39	−0·04	
44	7	218·38	218·8	+0·42	
45	8	231·53	231·79	+0·26	
45	10	245·19	245·28	+0·09	
47	10	259·15	259·91	+0·76	→Diff. goes on increasing with atomic number as shown in Fig. 4.
48	10	273·81	274·33	+0·52	
49	10	288·81	290·26	+1·45	

Atomic number (Z).	NO. of electrons in O_{II}, O_{III} level.	$\frac{\nu}{R}$ for L_{γ_4} [$L_I \rightarrow O_{II}$, O_{III}].	$\frac{\nu}{R}$ for L_I.	Diff. between L_I and L_{γ_4}.	
49	1	312·17	312·14	−0·03	
50	2	328·82	329·03	+0·21	
51	3	346·02	346·27	+0·25	
52	4	363·68	363·94	+0·26	
53		381·89	382·26	+0·37	
54	6	...	401·02	...	
55	6	420·11	421·79	+1·68	Diff. goes on increasing with (Z).
56	6	439·91	441·9	+2·0	
57	6	460·54	462·85	+2·13	

The agreement between the ν/R values of the emitted and the absorbed quanta given in the above tables (I and II) seems to be fairly satisfactory if it is taken into consideration that the accuracy of the measurement of the absorption limits is not as good as that of the lines and that different values of the same limit are given by different experimenters.



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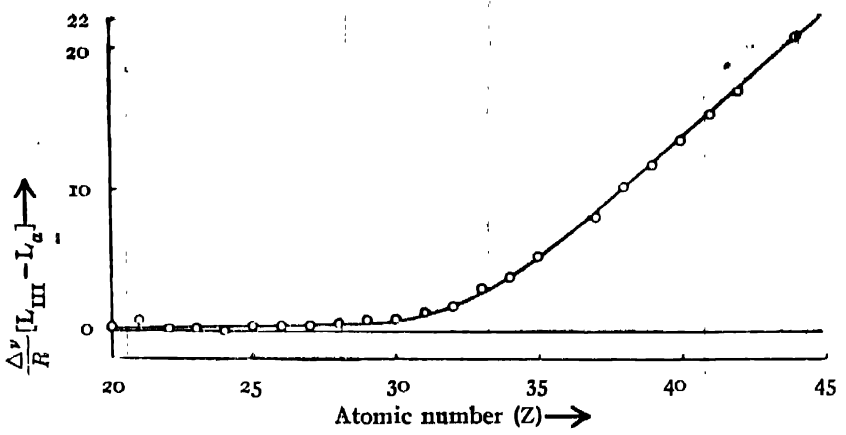

FIGURE 6.

Next, let us consider the $L\alpha$ lines from Ca(20) to elements of higher atomic number. Figure 5 shows a relation between the wave-length difference between $L\iota$ and $L\alpha$ lines and atomic number. This curve is of surprising appearance and exhibits a marked discontinuity at Cr(24). The relation between the difference between ν/R values of L_{III} and $L\alpha$ as a function of atomic number is shown in figure 6. In table III are given these values.

TABLE III.

Atomic number (Z).	Number of electrons in M_{IV}, M_V level.	$\frac{\nu}{R}$ of L_α [$L_{III} \rightarrow M_{IV}\, M_V$].	$\frac{\nu}{R}$ of L_{III}.	Diff. between L_{III} and L_α.	Remarks.
20	...	25·2	25·59*	+0·39	* Prins and Taken's [5] experimental values of L_{II}, L_{III} for Ca(20) and Ti(22) and of L_{III} for Cu(29).
21	1	29·1	29·9	+0·8	
22	2	33·26	33·41*	+0·15	
23	3	37·7	37·9	+0·2	
24	5	42·3	42·3	0	
25	5	47·0	47·3	+0·3	
26	6	51·8	52·2	+0·4	
27	7	57·2	57·7	+0·5	
28	8	62·7	63·2	+0·5	
29	10	68·5	69·3*	+0·8	Diff. goes on increasing with (Z) as shown in Fig. 6.
30	10	74·51	75·4	+0·9	
31	10	80·86	82·18	+1·32	
32	10	87·50	89·3	+1·8	

In this case the experimental values[5] of L_{III} are only for Ca(20), Ti(22), and Cu(29). For other elements, besides these three, computed values of L_{III} are used from Siegbahn's Spectroskopie Der Röngenstrahlen (2nd. Ed., 1931). In the case of Ga(31), L_{III} has been computed from $(K-K\alpha_1)$, where the experimental value of K given by Kievit and Lindsay [6] has been adopted. Their value of the K limit of Ga seems to be more correct than that of others as has been emphasised and experimentally verified very recently by Mutch. [7] From Rb(37) onwards the experimental values of L_{III} have been utilised. In the case of Ca and Ti the experimental values are of L_{II}, L_{III}; this means that actual values of L_{III} will be still less and, therefore, the agreement between the absorbed and emitted quantum may be expected to be still better.

On the whole, the agreement is not far from satisfactory if the widths of the emission lines in this region, are also taken into consideration. It would be quite interesting to photograph suitable absorption limits and the L_α lines in this region on the same photographic plate. It may be also possible that the L_{III} electrons, for the non-metals, instead of going to the first unoccupied or incompletely filled up orbit, goes to optical levels as has been also suggested by Mukerjee and Ray.[8] If this is so then the L_α lines for them are due to transitions from the optical levels to the L_{III} level. Therefore, the main point seems that these so-called semi-optical lines are due to transitions of electrons from that particular

level (may it be the first unoccupied or partly occupied orbit or an optical level, or conduction level) where the knocked out electron from the inner level, lodges itself.

Although the above view may hold good, as the agreement between the emitted and the absorbed quantum is quite good in some cases, there remains also a slight difference in some of them ; and this departure has, perhaps, got a significance like this. We should take into consideration that the experimental values of wave-lengths are obtained not from free atoms but from metallic crystals which according to Kroning [9] consist of permitted and forbidden energy zones of definite width. Also according to conduction theory of metals [10] the incomplete number of electrons in a level (valence level) of an atom, form the lower of the energy zones common to all the atoms of the crystal lattice. Thus, due to this definite width of these zones, (and not sharp quantum levels of atoms) the probability of the absorbed energy of the ejected electron from the inner level lodging itself in a permitted zone being equal to that of the emitted energy due to the electron jump from the same permitted zone, may not be expected to hold good.

K Series :

Kievit and Lindsay [6] have shown experimentally that the $K\beta_2$ ($K \rightleftharpoons N_{II}$ N_{III}) line of Cu(29) coincides exactly with the principal K limit of Cu and have ascribed most of the K limits of elements from Cr(24) to Zn(30) to the transfer of electrons from the K levels to N_{II} levels of the elements, the N_{II} level being vacant for these elements. This is, therefore, a very strong support of the view that an emission line having a transition from a vacant level of an atom is due to the electron jump from the level which has already captured the electron ejected from an inner level by the absorption of energy.

The relation between the difference of ν/R values of K limits and $K\beta_1$ lines and the corresponding atomic numbers is shown in figure 7. Figure 8 shows the same thing for $K\beta_2$ for the corresponding elements.

In Table IV are given these values.

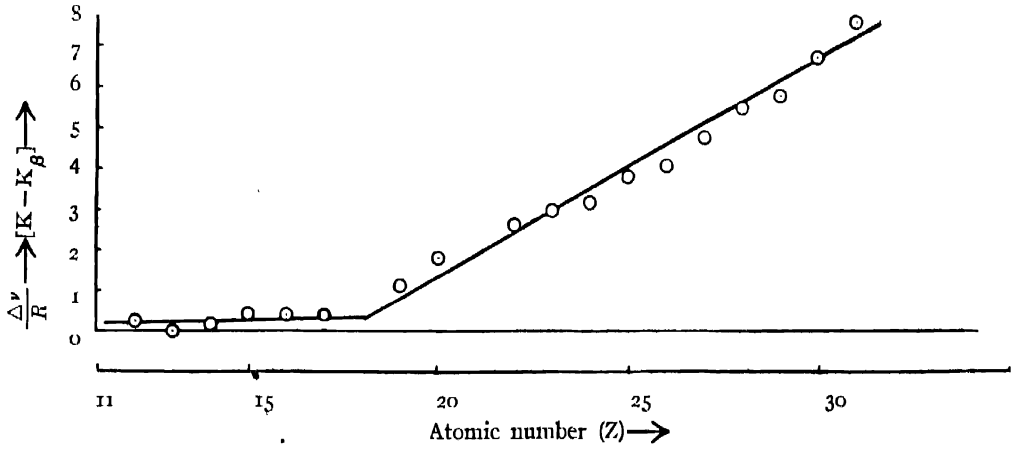

FIGURE 7.

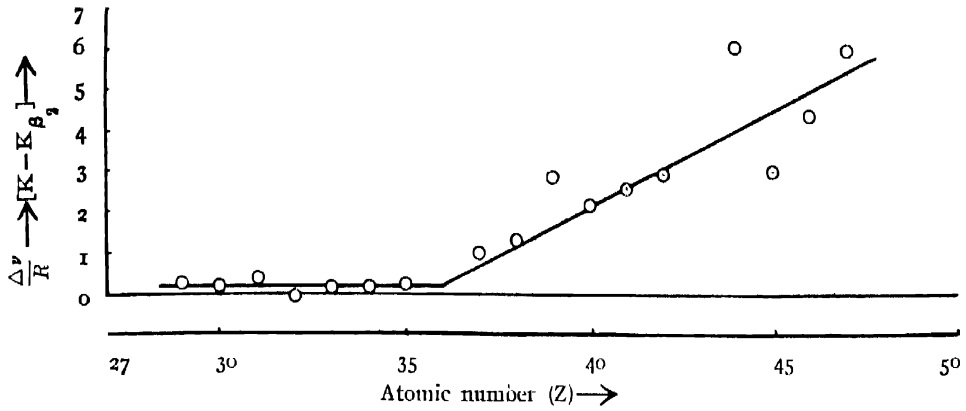

FIGURE 8.

TABLE IV.

Atomic number (Z)	Number of electrons in M_{II} M_{III} level	ν/R for $K\beta_1$[K ⟷ M_{III}]	ν/R for K	Diff. between K and $K\beta_1$	Remarks.
12	...	95·57	95·8*	+0·23	*Taken from Sommerfeld's Atomic Structure and spectral lines [Third Edition, Revised, 1934].
13	1	114·76*	114·84	+0·08	
14	2	135·21*	135·38	+0·17	
15	3	157·41*	157·80	+0·39	
16	4	181·49	181·90	+0·41	
17	5	207·36	207·8	+0·44	
18	6				
19	6	264·38	265·60	+1·22	Diff. goes on increasing with (Z) as shown in Fig. 7.
20	6	295·54	297·38	+1·84	
21	6	328·52	331·17	+2·65	
22	6	363·20	365·80	+2·60	

Atomic number (Z)	Number of electrons in N_{II} N_{III} level	ν/R for $K\beta_2$[K ⟷ N_{III}]	ν/R for K	Diff. between K and $K\beta_2$	Remarks.
28	...	613·40	613·85*	+0·45	*Kievit and Lindsay's [6] value.
29	...	661·30	661·59	+0·29	
30	...	711·34	711·67	+0·33	
31	1	763·34	763·68*	+0·34	
32	2	817·58	817·57	−0·01	
33	3	873·86	874·01	+0·15	
34	4	931·85	932·0	+0·15	
35	5	992·39	992·57	+0·18	
36	6				Diff. goes on increasing as shown in Fig. 8.
37	6	1118·45	1119·4	+0·95	
38	6	1184·69	1186·0	+1·31	

The $K\alpha$ lines Li(3), Be(4), etc., are also semi-opticals in the sense that the $L_{II}L_{III}$ level is in a state of development from B(5) and there is no electron at all in $L_{II}L_{III}$ level for Li and Be. The $K\alpha$ lines for these elements are bands and have a width extending to several A.U. and consisting of, besides the main peak, many other maxima. The electron transition of these lines takes place from conduction levels, as suggested by O'Bryan and Skinner;[11] and therefore, the difference between the absorbed and the emitted quanta for the K level and the $K\alpha$ lines for these elements becomes more significant which is evident from the complications arising from the width of the conduction levels.

M Series :

The agreement between the ν/R values of M_{III} limit and the line ($M_{III} \leftrightarrow O_{IV}$) from the elements Lu(71) to Au(79) has also been shown by Sandstrom. The corresponding ν/R values of M_V limit and $M\alpha_1$($M_V \leftrightarrow N_{VII}$) lines from Ce(58) onwards are given below in Table V.

TABLE V.

Atomic number (Z)	Number of electrons in N_{VI} N_{VII}	ν/R of $M\alpha_1[M_V \longleftrightarrow N_{VII}]$	ν/R of M_V	Diff. between M_V and $M\alpha_1$	Remarks.
58	1	64·95	65·4	+0·45	
59	2		68·8		
60	3	72·04	72·5	+0·46	
61	4				
62	5	79·89	79·8	−0·09	
63	6	83·36	83·8	+0·44	
64	7	87·67	87·7	+0·03	
65	8	91·89	91·7	−0·19	
66	9	95·68	95·8	+0·12	
67	10	99·67	99·7	+0·03	
68	11	103·75	104·1	+0·35	
69	12				
70	13	112·20	112·9	+0·7	Diff. goes on increasing with (Z).
71	14	116·47	117·4	+0·93	
72	14	121·12	122·7	+1·58	
73	14	125·92	127·8	+1·88	

The values of ν/R for M_V used in the above table V, are computed ones. That there is a discrepancy, due to combination defect, between the computed and the experimental values for M_{III} and M_V levels, has been stressed by Siegbahn.[12] But this discrepancy does arise in the case of M_V and M_{III} from W(74) to U(92).

CONCLUSION

Although it is only in some cases that the energy of the absorbed quantum has agreed almost exactly with that of a corresponding semi-optical line, the difference in the corresponding ν/R values is never, of course, greater than 0·2 on the average in most of the cases. Also the discontinuity of all the particular curves shown, at the atomic number where the level in question is first completely filled up, gives justification in differentiating these so-called semi-optical lines from other X-ray lines. Lastly, it is to be mentioned that the photograph of some of these lines and some of the corresponding absorption limits (as has been done by Kievit and Lindsay [6] in cases of $K\beta_2$ of Cu and indirectly by Kawata [4] in the case of $L_I\beta_5$ of W and Pt on the same plate, will be more interesting and in a sense decisive. It will also throw more light on the process of absorption in these cases.

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